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TECHNICAL REPORT ARCSL-TR-78057

PREDICTING THE DROPLET SIZE AND YIELD FACTORS OF A PHOSPHORUS SMOKE AS A FUNCTION OF DROPLET COMPOSITION AND AMBIENT RELATIVE HUMIDITY UNDER TACTICAL CONDITIONS

by

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November 1978

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARCSL-TR-78057	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* PREDICTING THE DROPLET SIZE AND YIELD FACTORS OF A PHOSPHORUS SMOKE AS A FUNCTION OF DROPLET COMPOSITION AND AMBIENT RELATIVE HUMIDITY UNDER TACTICAL CONDITIONS		5. TYPE OF REPORT & PERIOD COVERED Technical Report January 1978–June 1978
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Glenn O. Rubel		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Commander/Director, Chemical Systems Laboratory Attn: DRDAR-CLB-P Aberdeen Proving Ground, Maryland 21010		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project 1T161102A71A
11. CONTROLLING OFFICE NAME AND ADDRESS Commander/Director, Chemical Systems Laboratory Attn: DRDAR-CLJ-R Aberdeen Proving Ground, Maryland 21010		12. REPORT DATE November 1978
		13. NUMBER OF PAGES 47
14. MONITORING AGENCY NAME & ADDRESS*(If different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

(U)	Condensation nuclei	Phosphoric acid	Theory	Solutions
	Surface tension	Thermodynamics	Predictions	Condensation
	Distribution function	Particle size	Smoke	Growth
	Relaxation time	Water vapor	Drops	Diffusion

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

(U)   The equilibrium vapor pressure over the surface of a droplet containing an aqueous solution of volatile solvent and nonvolatile solute is uniquely determined by the Kelvin and solute effects. A general thermodynamic relationship is developed for the equilibrium vapor pressure (saturation ratio) over the surface of a droplet as a function of diameter and droplet composition (solute and solvent). From the general relationship, a particular expression is formulated for the saturation ratio over the surface of a phosphoric acid droplet as a function of droplet diameter and moles of acid

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20.   ABSTRACT (Contd)

contained by the droplet. It is assumed that vapor diffusional equilibrium exists between the surface of the acid droplet and the environment under tactical conditions. Consequently, a predictive relationship between the ambient relative humidity and the diameter of a phosphoric acid droplet follows. With this relationship, numerical values for the droplet diameters of a representative phosphorus smoke are generated for environmental relative humidities ranging from 10% to 98%. The representative phosphorus smoke is characterized by a mole spectrum of condensation nuclei ranging from 0.30×10^{-15} to 0.14×10^{-12} moles or, equivalently, a diameter spectrum varying from 0.30 to 2.5 μm. To verify the validity of diffusional (vapor) equilibrium, an investigation on the kinetics of condensational growth is executed. With the introduction of the "modified" growth law, a discussion on bounded and unbounded growth is presented. An analytical solution (droplet radius as a function of time) is offered for the growth equation as applied to the physical phenomenon of bounded growth. In the course of this development, relaxation times, representing the time for approach to equilibrium, are established. Numerical values for relaxation times are computed as applied to the "representative" phosphorus smoke for growth toward equilibrium under relative humidities ranging from 10% to 98%. With these results, implications of the assumption of diffusional equilibrium are suggested.

A chemical "pathway" is offered for the creation of phosphoric acid droplets from elemental phosphorus. Based on this model, a theoretical expression for the yield factors of a phosphorus smoke is established. Numerical values indicate that yield factors are highly dependent on the environmental relative humidity.

PREFACE

The work described in this report was authorized under Project 1T161102A71A, Scientific Area 05, Aerosol/Obscuration Science. This work was started in January 1978 and completed in June 1978.

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Acknowledgments

The author wishes to acknowledge the technical contributions of Dr. Edward Steubing and Dr. Gerald Holst in the fields of physical chemistry and computer sciences. I would also like to thank Dr. J. C. Carstens for technical advisement in the area of cloud physics.

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PREDICTING THE DROPLET SIZE AND YIELD FACTORS OF A PHOSPHORUS SMOKE AS A FUNCTION OF DROPLET COMPOSITION AND AMBIENT RELATIVE HUMIDITY UNDER TACTICAL CONDITIONS

I.   INTRODUCTION.

The development of a particle size prediction model satisfies two basic informational needs of aerosol physicists: first, the prediction model provides a means for characterizing the physical properties of particles comprising an aerosol; secondly, the model illustrates possible avenues toward the aim of artificial particle size control.

The goal of this study is threefold: (1) To develop a predictive relationship between the size of a phosphoric acid droplet and the ambient relative humidity. (2) To explore the kinetics of condensational growth toward stable equilibrium and to investigate the validity of the assumption that vapor diffusional equilibrium exists between the environment and the surface of the phosphoric acid droplet under tactical conditions. (3) To formulate a predictive relationship between the yield factors of a phosphorus smoke and the relative humidity.

In order to realistically model the growth and predict the droplet size of an aerosol such as phosphorus, several physiochemical processes must be investigated. However, due to the hygroscopic nature of the phosphorus oxides and their tendency to generate solution droplets, one such process, condensation-evaporation, assumes a dominant role in the determination of the droplet size under tactical conditions.

The analysis of solution droplets has received a considerable amount of attention from such researchers as Byers,[1] Low,[2] and Friedlander.[3] To effectively analyze the relationship between vapor condensation and the size of a phosphoric acid droplet, a combination of equilibrium thermodynamics and aerosol kinetics is employed. With data for the water activity, surface tension, and density of phosphoric acid solutions, the droplet (phosphoric acid) saturation ratio is formulated from basic thermodynamic considerations. By applying the Kelvin and solution effect to a phosphoric acid droplet, the droplet saturation ratio is explicitly expressed as a function of droplet diameter and acid content. To incorporate the solution effect, an empirical relationship between the water activity and water mole fraction of a phosphoric acid solution is formulated. Vapor diffusional equilibrium is assumed between the surface of the phosphoric acid droplet and the environment whereupon a predictive relationship between relative humidity and droplet diameter follows.

To verify the validity of vapor diffusional equilibrium, the kinetics of condensational growth is explored. Employing the modified growth law developed by Carstens,[4] a quasi-steady state analysis based upon a balance between heat conduction and vapor condensation, the growth of a phosphoric acid nucleus can be delineated. The growth law is modified to apply to the growth regimes dominated by molecular and continuum phenomenon. From the modified growth law, relaxation times (times for growth toward stable equilibrium) are constructed. Numerical results indicate that phosphoric acid droplets "track" with the environment.

Subsequently, yield factors for a phosphorus smoke are displayed.

II. RELATIONSHIP BETWEEN THE SATURATION RATIO AND DIAMETER OF A SOLUTION DROPLET.

In order to establish the relationship between the relative humidity and droplet diameter, the vapor (water) saturation ratio over a droplet containing a nonvolatile, soluble, dissociating solute must be developed. Theoretically, if the saturation ratio of the environment is equal to 1, that is,

$$S_e = \frac{P}{P_{SO}} = 1 \longrightarrow P = P_{SO} \tag{1}$$

where

S_e = environmental saturation ratio, alternatively referred to as the ambient relative humidity

P = actual vapor pressure of the environment

P_{SO} = equilibrium vapor pressure determined by the temperature of the environment, vapor pressure over a plane surface of pure water

then liquid-phase water should coexist in equilibrium with gas-phase water. However, nucleation experiments indicate that water droplets will not form until the saturation ratio of the environment exceeds 3 ($P > 3\,P_{SO}$), an extremely supersaturated state.*

The reason for this discrepancy between experiment and theory can be explained in terms of the Kelvin effect. The Kelvin relation relates the vapor pressure over a curved surface to the vapor pressure over a plane surface of the same liquid and concludes that the vapor pressure over a curved surface is greater than the vapor pressure over a plane surface. From a physical viewpoint, the vapor pressure over a surface of liquid is determined by the energy necessary to separate a volatile molecule on the surface from the attractive forces exerted by its nearest neighbors located in the layer adjacent to the surface.[3] The attractive number ratio, defined by the ratio of the number of molecules in the layer adjacent to the surface (N_{s-1}) to the number of molecules in the surface layer (N_s), is smaller for the curved surface as compared to the plane surface. Consequently, the net energy of attraction is effectively reduced over the curved surface thereby augmenting the escaping tendency of the volatile molecules.

Mathematically, this relationship between vapor pressures may be given as:[1,2]

$$Ln\left(\frac{P_d}{P_s}\right) = \frac{4\sigma' M_1}{RT\rho' d} \tag{2}$$

---

*This is true only in the absence of foreign material.

where

P_d = vapor pressure over the curved surface characterized by diameter, d

P_s = vapor pressure over a plane surface

σ' = surface tension of the surface with units ergs/cm^2

ρ' = density of the solution droplet

M_1 = molecular weight of water

R = the universal gas constant

T = temperature of the system

The Kelvin law states that the natural logarithm of the ratio of the two vapor pressures is inversely proportional to the diameter of the droplet; all other terms are considered constant.* By transforming the Kelvin law into its exponential equivalent, it is clearly seen that $P_d > P_s$ for all diameters, d. The implications are that when the environmental vapor pressure is just able to sustain a plane surface of liquid ($S_e = 1$), it is not yet capable of sustaining a droplet with a curved surface. Only when the environment is supersaturated ($P > 3\,P_{so}$) can droplets exist in equilibrium. If this were the only phenomenon controlling the vapor pressure over a droplet containing a soluble nonvolatile solute, then the existence of a droplet in an unsaturated environment would be a thermodynamically impossible state. However, much air-quality degradation in unsaturated environments is due to droplet formation (haze) exemplified by sulfuric acid droplets.

The phenomenon that allows droplets to exist in equilibrium with an unsaturated environment is commonly referred to as the solute effect. The solute effect relates the vapor pressure over a plane surface of liquid with soluble, nonvolatile solute to the vapor pressure over a plane surface of liquid without solute. Because of the solute effect, the vapor pressure over a liquid with solute is less than the vapor pressure over a liquid without solute. The physical reasoning that supports this conclusion is as follows:

> Vapor pressure is primarily a colligative property** dependent on the relative number of water molecules available for entry into the gas phase. With the addition of solute molecules, the relative number of water molecules is effectively reduced; therefore, a reduction in vapor pressure consequently follows.[3]

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*In this study, variations in σ' and ρ' result in second-order variations in saturation ratios.

**This is strictly true for ideal solutions only.

In ideal solutions, the solute effect can be mathematically modelled by Raoult's law,

$$P_s = X_1 P_{so}$$ (3)

where

P_s = vapor pressure over a plane surface containing liquid with soluble, nonvolatile solute

X_1 = mole fraction of solvent (1)

P_{so} = vapor pressure over the pure liquid with plane surface

With the addition of solute molecules, the solvent mole fraction, X_1, is reduced from its maximum value of unity to some fractional value, thereby resulting in a proportionate reduction in the vapor pressure of the solution as inferred from equation (3). From past experimental work, data on the vapor pressure over a plane-surfaced solution of phosphoric acid and water has been amalgamated for a wide range of acid concentrations at 25°C.[5,6] The data indicate a greater vapor pressure reduction due to the addition of a given amount of solute as compared to the value predicted by Raoult's law and support the conclusion that phosphoric acid solutions are nonideal. The nonideality of the solutions may stem from two basic physical mechanisms: (1) the dissociation of H_3PO_4 in aqueous solution and a subsequent increase in the relative number of solute molecules and (2) molecular dipole-dipole interactions between H_3PO_4 and H_2O.

Nevertheless, the inappropriateness of Raoult's law as a model for phosphoric acid solutions is quite evident and obviates its application in this study.

A more cogent model for the solute effect in nonideal solutions can be mathematically represented by

$$P_s = X_{1eff} P_{so}$$ (4)

where X_{1eff}, the effective solvent mole fraction or water activity,[7] accounts for the nonideality of the solution.

Through a joint effort between Mr. Theodore Tarnove* and this author, the functional relationship between X_{1eff} and X_1 has been mathematically formulated for phosphoric acid solutions. In order to account for the total domain ($0 \leqslant X_1 \leqslant 1$), two straight-line fits were applied, resulting in the following relationship:

$$X_{1eff} = 2X_1 - 1 \qquad 1 \geqslant X_1 \geqslant .577$$

$$X_{1eff} = .22X_1 \qquad 0 \leqslant X_1 < .577$$

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*Tarnove, Theordore, Munitions Division, Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland 21010, February 1978, private communication.

The general expression for the saturation ratio over the droplet containing soluble dissociative nonvolatile solute is obtained by the substitution of equation (4) into equation (2), resulting in the following thermodynamic relationship:

$$\ln \frac{P_d}{P_{so}} = \frac{4\sigma' M_1}{RT\rho' d} - \ln \left[\frac{1}{X_{1eff}} \right] \tag{5}$$

III. SATURATION RATIO OVER PHOSPHORIC ACID DROPLETS.

For phosphorus smoke, the empirical relationships for X_{1eff} may be employed, along with the substitution $X_1 = \dfrac{n_1}{n_2 + n_1}$, where n_1 and n_2 are the number of moles of solvent and solute, respectively, thereby resulting in the multivalued functional form for the saturation ratio over the surface of phosphoric acid droplet, where:

$$\ln \frac{P_d}{P_{so}} = \frac{4\sigma' M_1}{RT\rho' d} - \ln \left[1 + \frac{2n_2}{n_1 - n_2} \right] \quad 1 \geqslant X_1 \geqslant .577 \tag{6}$$

$$\ln \frac{P_d}{P_{so}} = \frac{4\sigma' M_1}{RT\rho' d} - \ln \left[4.55 + 4.55 \frac{n_2}{n_1} \right] \quad .577 < X_1 \geqslant 0 \tag{7}$$

With the additional substitution, $\dfrac{\pi d^3}{6} = n_2 V_2 + n_1 V_1,$* which states that the total volume of the droplet is associated with the volume of the solute and the volume of the solvent, then equations (6) and (7) become with some mathematical simplification:

$$\ln \frac{P_d}{P_{so}} = \frac{4\sigma' M_1}{RTd\rho'} - \ln \left[1 + \frac{12 n_2 V_1}{\pi d^3 - 6 n_2 (V_2 + V_1)} \right] \quad 1 \geqslant X_1 \geqslant .577 \tag{8}$$

$$\ln \frac{P_d}{P_{so}} = \frac{4\sigma' M_1}{RTd\rho'} - \ln \left[4.55 + \frac{27.3 n_2 V_1}{\pi d^3 - 6 n_2 V_2} \right] \quad .577 > X_1 \geqslant 0 \tag{9}$$

---

*From density-data analysis, V_2 (the mole volume of H_3PO_4) and V_1 (the mole volume of H_2O) are reasonably constant over all degrees of acid-concentrated solutions.

The above particular expressions relate the saturation ratio over a phosphoric acid droplet, i.e., $S_d = \dfrac{P_d}{P_{so}}$, to the fundamental properties of that droplet, i.e., the diameter, d and the number of moles of acid n_2 contained in the droplet. The first term on the right (positive) represents a vapor pressure increase due to the Kelvin effect; and the second term, a subtractive expression, represents the vapor pressure reduction due to the solute effect.

With the approximation that the droplets contain dilute solutions, i.e., $\dfrac{\pi d^3}{6} >> n_2 V_2$, then the logarithmic term may be expanded in a Taylor series expansion retaining the first term only: $\ln(1 + X) = -X$ where $X << 1$. This circumstance would be applicable only to equation (8) where the mole fraction of solvent approaches unity and, therefore, with this approximation equation (8) becomes:

$$\ln \frac{P_d}{P_{so}} = \frac{4\sigma' M_1}{RT\rho' d} - \frac{12 n_2 V_1}{d^3} \tag{10}$$

This expression is referred to as the Köhler expression and is valid only for dilute solutions.[3] While it is not a good model for highly concentrated acid droplets, as in a phosphorus smoke, some valuable information may be gleaned from this expression. In particular, the competition between effect (the first term on the right) and the solute effect is clearly revealed as a function of diameter. For "small" diameters, the solute effect dominates the Kelvin effect, resulting in saturation ratios less than 1 (see figure 1). As the diameter increases and the solution becomes dilute, the two effects become equal in magnitude ($S_d = 1$) and thereafter the Kelvin effect dominates, resulting in a droplet saturation ratio greater than 1. As the diameter of the drop increases to infinity, both effects become negligible, physically representing a plane surface of pure liquid, whose saturation ratio equals 1.

To effectively model phosphorus smoke, consisting of concentrated phosphoric acid droplets, equations (8) and (9) will be employed for analysis.

To gain additional insight from equations (8) and (9), a graphical representation is displayed on a S_d versus diameter axes system for constant mole of solute. The result is a family of curves, each curve constrained by a fixed amount of solute.* This procedure has been applied to a phosphorus smoke where the moles of acid contained in each droplet has been determined in the following manner (see figure 1 and table 1).

Using a cascade impactor, measurement of acid droplet sizes at known relative humidity is performed; and with knowledge of the relationship between acid concentration of the solution and relative humidity, a determination of number of moles of solute contained in

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*In general, a two-component system has three degrees of freedom. By fixing temperature and amount of acid in each droplet, one degree of freedom remains: it is relative humidity.
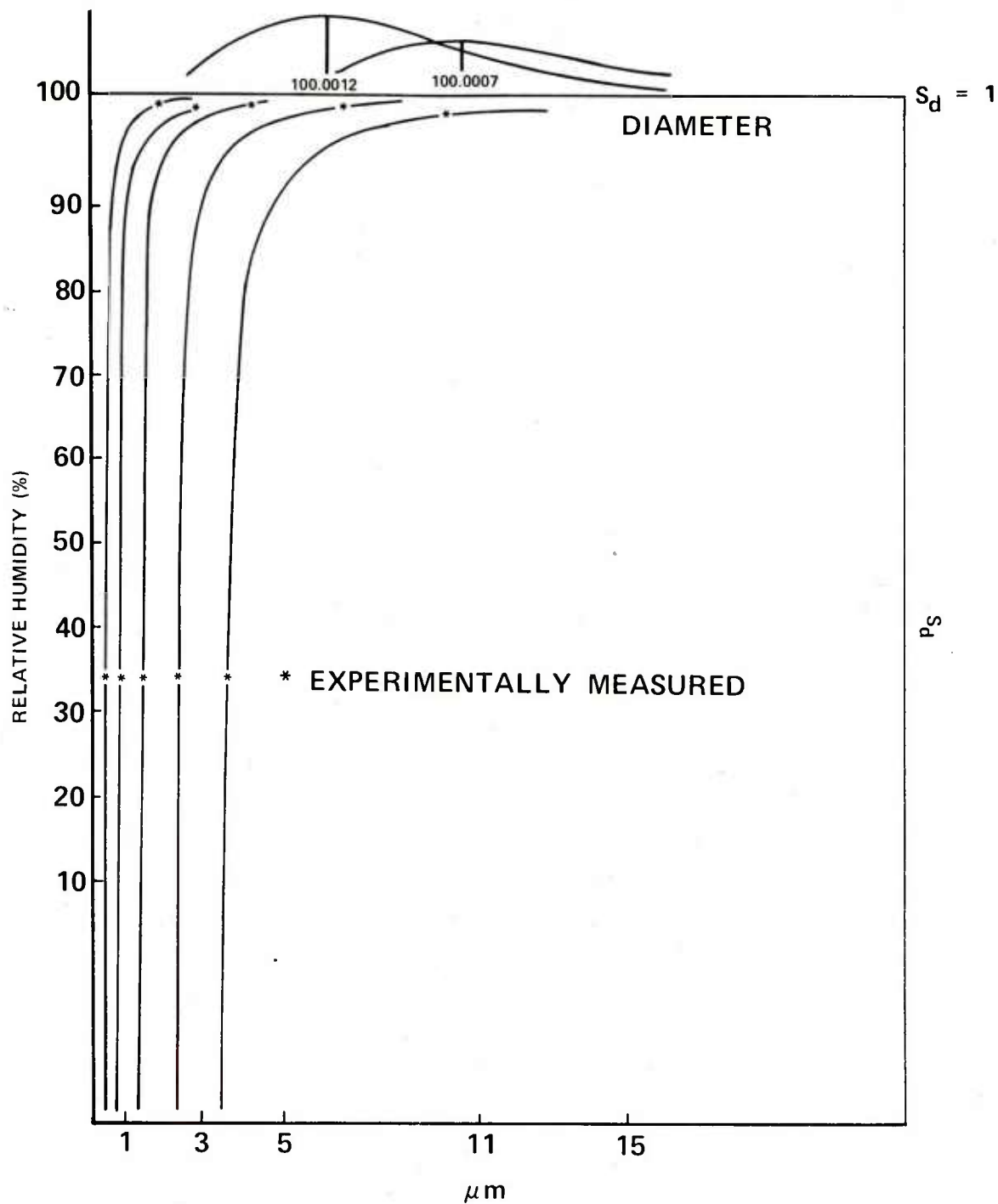
Figure 1. Equilibrium Diameter of Phosphoric Acid Droplets
As a Function of Relative Humidity

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*Tarnove, Theordore, Munitions Division, Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland 21010, February 1978, private communication.

Table 1. Equilibrium Diameter of Phosphoric Acid Droplets As a Function
of Relative Humidity (RH) and Condensation Nuclei Diameter (d_c)

d_c	N_2	RH 10%	20%	35.8%	40%	50%	60%	70%	80%	90%	98%
0.30 μm	.29E-15	.34 μm	.34 μm	.37 μm	.38 μm	.39 μm	.41 μm	.44 μm	.49 μm	.60 μm	.98 μm
0.47 μm	.10E-14	.50 μm	.54 μm	.56 μm	.57 μm	.59 μm	.62 μm	.66 μm	.74 μm	.91 μm	1.48 μm
0.80 μm	.5E-14	.86 μm	.92 μm	.96 μm	.97 μm	1.01 μm	1.06 μm	1.14 μm	1.27 μm	1.56 μm	2.56 μm
1.50 μm	.34E-13	1.64 μm	1.74 μm	1.82 μm	1.86 μm	1.91 μm	2.00 μm	2.16 μm	2.40 μm	2.96 μm	4.90 μm
2.40 μm	.14E-12	2.62 μm	2.78 μm	2.90 μm	2.94 μm	3.06 μm	3.22 μm	3.46 μm	3.86 μm	4.72 μm	7.84 μm

N_2 = MOLES OF SOLUTE (H_3PO_4)

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each droplet is made. For this study, the mole spectrum of H_3PO_4 varies from 0.30×10^{-15} to 0.14×10^{-12} moles. It will sometimes be more instructive to refer to a diameter spectrum for the acid nuclei, denoted by d_c; and for this study d_c varies from 0.30 to 2.5 μm. These quantities of acid will be considered as the condensation nuclei for further vapor diffusional growth. With reference to the generation of phosphorus smoke, after burning the elemental phosphorus and as the phosphorus pentoxide chemisorbs water vapor, condensation nuclei are generated. These condensation nuclei consisting of phosphoric acid will grow by vapor condensation until diffusional equilibrium with the environment is achieved. The "equilibrium states" are uniquely specified by equations (8) and (9).

IV. PHOSPHORIC ACID DROPLET DIAMETER AS A FUNCTION OF RELATIVE HUMIDITY.

At this point, a relationship between saturation ratio over the surface of a droplet and the droplet diameter has been developed; however, as stipulated in the introduction, the main objective is to obtain a relationship between relative humidity and droplet diameter. To achieve the stated objective, one additional statement needs to be furnished and that is: diffusional equilibrium exists between the surface of the droplet and the environment. This statement implies equivalence between S_e and S_d. However, S_e (the environmental saturation) is synonymous with relative humidity; therefore, through transitive association, the relationship between S_d and d is identical to the relationship between RH and d, and the desired goal has been accomplished.

With this final identification, the predictive relationships between relative humidity and phosphoric acid droplet diameter are expressed as,

$$\ln \psi = \frac{4\sigma'M_1}{RTd\rho'} - \ln \left[1 + \frac{12\,n_2 V_1}{\pi d^3 - 6\,n_2(V_2 + V_1)} \right] \quad 1 \geqslant X_1 \geqslant .577 \qquad (8a)$$

$$\ln \psi = \frac{4\sigma'M_1}{RTd\rho'} - \ln \left[4.55 + \frac{27.3\,n_2 V_1}{\pi d^3 - 6\,n_2 V_2} \right] \quad .577 > X_1 \geqslant 0 \qquad (9a)$$

where ψ is the relative humidity (RH). After specifying the constants σ', M_1, R, T, ρ', V_1, V_2, and the moles of acid (n_2) of the condensation nucleus, the phosphoric acid droplet diameter is evaluated as a function of relative humidity. *Therefore, with knowledge of the condensation nuclei size distribution of an oxidized phosphorus smoke, the phosphoric acid droplet size distribution can be predicted from the environmental relative humidity.*

Scrutiny of table 1 reveals the following salient features of the thermodynamic properties of H_3PO_4 droplets. First, *the relative increase in droplet diameter is independent of the initial condensation* nucleus diameter. The relative diameter increase is represented by the ratio d_ψ/d_c, where d_ψ is the diameter of the H_3PO_4 droplet at the specified relative humidity

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and d_c is the diameter of the particular condensation nucleus instigating growth. From the numerical results of table 1, calculations for d_ψ/d_c at various ψ's reveal that the ratio is only dependent on ψ and not on d_c. *Roughly, the relative increase in droplet diameter takes on the values 1.5, 2, and 3 for relative humidities 70%, 90%, and 98%, respectively, for all condensation nuclei of the representative phosphorus smoke.* The physical reasoning supporting this conclusion is that for the smoke in interest the solute effect dominates the Kelvin effect. Furthermore, the solution effect acts to dilute all droplets to a uniform extent. Since the ratio, d_ψ/d_c, is a parameter of dilution and all droplets achieve the same degree of dilution then all droplets experience the same relative increase in droplet diameter, irrespective of initial condensation nucleus size.

Secondly, *the change in droplet diameter concomitant with a change in relative humidity is a monotomically increasing function of relative humidity and the greatest proportion of growth occurs in the region defined by $\psi > 80\%$*; more mathematically,

$$\partial d/\partial \psi = H(\psi) \uparrow$$

A cursory mathematical justification for the "accelerated" growth of droplets with increasing relative humidity can be developed from inspection of the Köhler expression. For high humidities, the phosphoric acid droplets become dilute and the Köhler expression is an appropriate model for phosphorus smoke. Nevertheless, recalling that S_d is equivalent to ψ at equilibrium, the dependence of ψ on d is concluded to be inversely proportional. Basic differentiation of ψ with respect to d reveals that the slope of this expression, $\partial \psi/\partial d$, is inversely proportional to droplet diameter. The rate of change of droplet diameter with respect to relative humidity, $\partial d/\partial \psi$, obtained by simple inversion of $\partial \psi/\partial d$ is therefore *directly* proportional to droplet diameter. However, droplet diameter is a monotomically increasing function of ψ and $\partial d/\partial \psi$ is concomitantly an increasing function of relative humidity, ψ.

Finally, *it is noteworthy to realize that with knowledge of the droplet diameter, d, and the moles of acid, n_2, in the droplet, the droplet acid concentration can be calculated once the relative humidity is specified* (see appendix C). Information on the droplet acid concentrations would provide some information on the optical properties of the phosphorus smoke since acid concentration is tightly linked to index of refraction.

V. APPROXIMATION FORMULAE FOR PHOSPHORIC ACID DROPLET DIAMETER AS A FUNCTION OF RELATIVE HUMIDITY.

As formulated in Section IV, explicit relationships for the environmental relative humidity as a function of droplet diameter and number of moles of acid (n_2) have been developed mathematically, $\psi = \psi(d, n_2)$. The relationships take the form:

$$\ln \psi = \frac{4\sigma' M_1}{RT\rho' d} - \ln \left[1 + \frac{12 n_2 V_1}{\pi d^3 - 6 n_2(V_2 + V_1)} \right] \qquad 1 \geqslant X_1 \geqslant .577 \qquad (11a)$$

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$$\ln \psi = \frac{4\sigma' M_1}{RT\rho' d} - \ln \left[4.55 + \frac{27.3 n_2 V_1}{\pi d^3 - 6 n_2 V_2} \right] \qquad .577 > X_1 \geqslant 0 \qquad (11b)$$

Clearly, in equations (11a) and (11b) the droplet diameter, d, assumes the role of the independent variable and the relative humidity ψ, the dependent variable. In other words, by first establishing the diameter, the relative humidity is subsequently known. However, in reality, the relative humidity assumes some value independently of the smoke and the droplet diameter is established once ψ is specified. Therefore, a functional expression, formatted with ψ and d as the independent and dependent variable respectively, is physically more meaningful. To obtain this expression, equations (11a) and (11b), transcendental equations in diameter, must be mathematically inverted.

Unfortunately, equations (11a) and (11b) cannot be inverted analytically, so an approximate explicit relationship for the droplet diameter must suffice.

As concluded in Section IV, the solution effect governs the thermodynamic properties of a phosphoric acid droplet and solely determines the structure of the relationship between droplet diameter, d, and droplet saturation ratio, S_d. In phosphoric acid droplets the solution effect is mathematically modelled by

$$S_d = 2 X_1 - 1 \qquad (12)$$

where S_d and X_1 are as previously defined.

Applying the substitutions, $X_1 = n_1/(n_1 + n_2)$ and $\frac{\pi d^3}{6} = n_2 V_2 + n_1 V_1$, to equation (12) results in

$$S_d = (\pi d^3 - 6 n_2 V_2 - 6 n_2 V_1)/(\pi d^3 - 6 n_2 V_2 + 6 n_2 V_1) \qquad (13)$$

Equation (13), an "equation of state" for the properties of a phosphoric acid droplet, provides the defining relationship between S_d and d.

With the additional substitution, $n_2 = \pi \rho_c d_c^3/(6 M_2)$, where ρ_c and M_2 are the density and molecular weight, respectively, of phosphoric acid, a solution for d/d_c is obtained from equation (13). It is

$$d/d_c = (\rho_c/M_2)^{1/3} \left[\left(V_1(1 + S_d) + V_2(1 - S_d) \right)/(1 - S_d) \right]^{1/3} \qquad (14)$$

For the phosphoric acid-water system, the following data are relevant:

$$\rho_c = 1.87 \text{ g/cc}$$

$$M_2 = 98 \text{ g/cc}$$

$$V_1 = 18 \text{ cc/mole}$$

$$V_2 = 52.4 \text{ cc/mole}$$

Furthermore, once the droplet attains equilibrium with the environment, S_d is equal to ψ, and equation (14) becomes

$$d/d_c = 1.1030 \left[(1. - 0.4886 \, \psi)/(1. - \psi) \right]^{1/3} \tag{15}$$

Equation (15) is an approximate explicit relationship for the phosphoric acid droplet diameter as a function of relative humidity and condensation nucleus diameter. Comparison of exact and approximate diameters, calculated through equations (11) and (15), respectively, indicates, at most, a 2% error. The extremely close agreement corroborates the conclusion that the solution effect indeed governs the properties of a phosphoric acid droplet in a phosphorus smoke.

Examination of equation (15) reveals the independence of the relative increase in diameter (d/d_c) on the condensation nucleus diameter (d_c). Additionally, d/d_c increases monotomically with ψ and as $\psi \rightarrow 1$ the increase rises sharply, emphasizing the point that the greatest proportion of growth occurs in the region defined by $\psi \geqslant 80\%$.

Sensitivity of the particle size distribution function on relative humidity can be investigated with knowledge of the diameter approximation formula. Consider the following illustration.

As elemental phosphorus is burned, particle nucleation occurs giving rise to a ln-normal distribution for the condensation nuclei.* The distribution is given by

$$f(\ln d_c) = \frac{1}{(2\pi)^{1/2} \sigma g} \exp \left[- (\ln d_c - \ln d_{cg})^2 / 2 \, \sigma_g^2 \right] \tag{16}$$

where

$f(\ln d_c)$ = relative number of condensation nuclei with diameters between $\ln d_c$ and $\ln d_c + \Delta \ln d_c$

σ_g = geometric standard deviation

d_c = diameter of condensation nucleus

d_{cg} = geometric number mean diameter of distribution

As the condensation nuclei grow, the original distribution changes until equilibrium is reached with the environmental relative humidity. The approximation formula contains the

---

*Test chamber experiments on oxidized phosphorus indicate that the condensation nuclei are characterized by a ln-normal distribution.

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information that determines the manner in which the distribution varies. By simple substitution of equation (15) into equation (16), the new size distribution of droplet diameters is given by

$$f(\ln d) = \left[(2\pi)^{1/2} \sigma g \right]^{-1} \exp \left[-\ln d - \ln(a(\psi)d_{cg})^2 / 2 \sigma g^2 \right] \qquad (17)$$

where $a(\psi) = 1.1030[(1. - 0.4886\psi)/(1. - \psi)]^{1/3}$

       Equation (17) represents the size distribution function of a phosphorus smoke as a function of relative humidity and demonstrates two salient points.

       1.   The standard deviation (σg) of the distribution is invariant to changes in relative humidity. Therefore, the distribution retains its structure or shape through condensational growth.

       2.   The central tendency or geometric mean diameter increases from d_{cg} to $a(\psi)d_{cg}$ and results in a translation of the size distribution toward larger droplet diameters.

VI.   KINETICS OF CONDENSATIONAL GROWTH OF PHOSPHORIC ACID DROPLETS: RELAXATION TIMES.

       As stated earlier, diffusional equilibrium is established when the environmental saturation ratio (relative humidity) is equivalent to the droplet saturation ratio. Furthermore, the linchpin in the development of the relationship between relative humidity and droplet diameter is the adoption of diffusional equilibrium between the environment and H_3PO_4 droplet. To test the validity of this assertion, an investigation on the kinetics of condensational growth is warranted. More specifically, development of a relaxation time will provide the information needed to answer the question: Is diffusional equilibrium a reasonable assumption under tactical conditions?

       When inequality exists between the saturation ratios, a gradient in vapor concentration is developed, resulting in vapor diffusion toward the low concentration region. Kinetic growth or decay results until equality of the saturation ratios is once again established. Before launching into a quantitative analysis on the kinetics of condensational growth, it is instructive to illustrate some qualitative features of this nonequilibrium phenomenon. More specifically, with information on the properties of a droplet and the environmental relative humidity, conclusions concerning growth or decay may be ascertained.

       With reference to figure 2, a representative equilibrium curve is diagrammed with the impressed external condition of an unsaturated environment, i.e., $S_e < 1$. For convenience, consider a continuous distribution of droplets along the curve, each with its characteristic saturation ratio defined by the curve. Then one, and *only* one, droplet along this curve will be in equilibrium with the environmental relative humidity defined by the intersection of S_e and S_d. This intersection represents the condition for equality of the saturation ratios which is equivalent to diffusional equilibrium. For those droplets distributed along the lower portion of the curve, below S_e, the characteristic droplet saturation ratios are less than the environmental saturation ratio. Vapor diffusion toward the droplets occurs, resulting in condensational growth until their diameters correspond to the equilibrium diameter for that environment. For those droplets distributed along
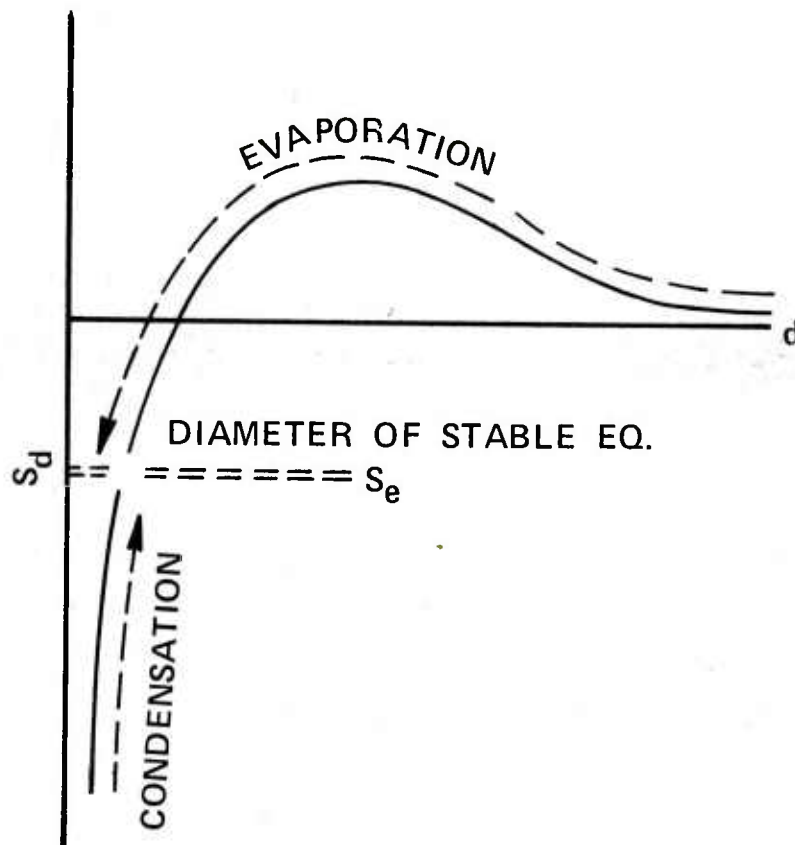
BOUNDED GROWTH

Figure 2. Kinetics of Approach to Equilibrium by an
Aerosol in an Unsaturated Environment

the upper portion of the curve, $S_d > S_e$, evaporation will result until they arrive at the equilibrium diameter, α_1. It is a simple matter to envision a family of curves, each possessing an "equilibrium" diameter, thereby generating a collection of equilibrium diameters for the given environment.

The same analysis may be applied to figure 3 where the external constraint is a supersaturated environment. Now two equilibrium diameters are present (two intersections): α_1 and α_2. However, these equilibrium diameters are distinct not only in size but also in nature. The smaller diameter, α_1, is designated a stable equilibrium point, whereas α_2 is referred to as an unstable equilibrium diameter.[4] The basis for these distinctions may be explained as follows: Consider a droplet with diameter α_1, if displaced upward along the curve, holding S_e constant, an evaporation process shall result until equilibrium is once established at α_1. Conversely, if displaced downward, then condensation occurs until equilibrium is restored. Therefore, with any displacement from equilibrium diameter α_1, a restoring force is established in the form of differential saturation ratios. The same analysis reveals that for any displacement from α_2, a driving force away from equilibrium is established, thereby arriving at the nomenclature of an unstable equilibrium diameter. Of special interest is the phenomenon of free growth resulting from a displacement away from the equilibrium diameter α_2 toward larger diameters. When this occurs, holding S_e constant, the droplet may freely grow by condensation, resulting in unbounded growth toward "giant" diameters. For the representative phosphorus smoke the supersaturation ratio is only .12%, an extremely small value for the initiation of free growth.

To further the understanding of condensational kinetics, a quantitative analysis is in order. Information on the time for approach to equilibrium is of considerable importance and illuminates the problem of diffusional equilibrium. The parameter which characterizes this time is designated the relaxation time, τ, and may be introduced through the modified diffusional growth law equation (18).

$$(a + \ell) \, da/dt = \rho_{eq}^{(\infty)} \, D_{eff} \, (S_e - S(a)/\rho_\ell \tag{18}$$

where

a = instantaneous radius of the droplet

ℓ and D_{eff} = surface effect parameters introduced to generalize the growth law for the transition region between molecular and continuum phenomenon

$\rho_{eq}^{(\infty)}$ = equilibrium vapor density of the environment at that temperature

ρ_ℓ = density of the diffusing vapor

t = time
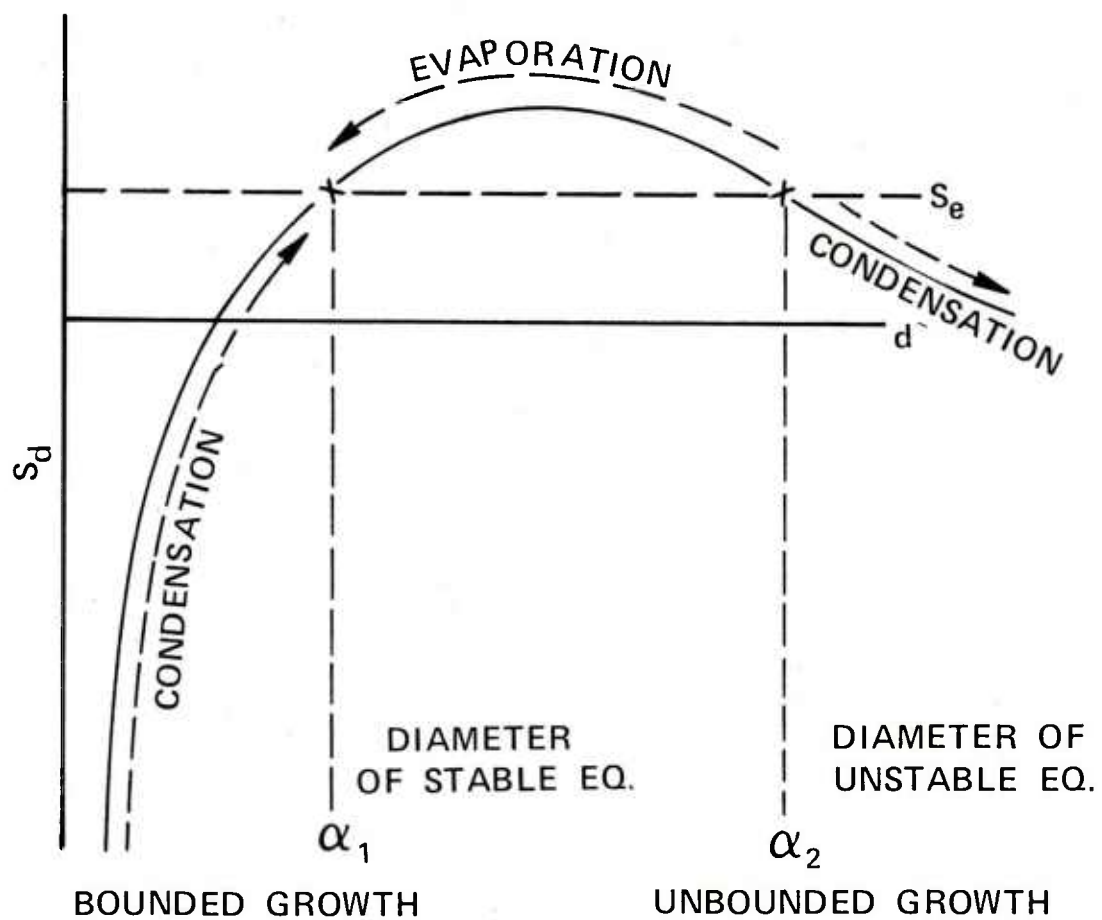
Figure 3. Kinetics of Approach to Equilibrium by an
Aerosol in a Super Saturated Environment

The modified growth law developed by Carstens *et al.*[4] represents a balance between vapor diffusion and heat conduction enveloped within a quasi-steady state analysis. Expressions for the surface effect parameters have been developed by Carstens involving the condensation coefficient α and the evaporation coefficient β. For this study, the values $\alpha = 1.0$ and $\beta = 0.5$ have been employed.

The solution to the first-order differential equation, a(t), is in general difficult to achieve analytically. However, for the constraint growth toward stable equilibrium, an approximate analytical solution may be displayed.

Mathematical reforming of equation (18) results in

$$t(a) = \frac{\rho \ell}{\rho_{eq}^{(\infty)} D_{eff}} \int_{a_O}^{a} \frac{(a' + \ell)da'}{S_e - S(a')} \tag{19}$$

where

$$a_O = \text{initial radius}$$

$$t(a) = \text{time at which the droplet achieves final radius } a$$

With substitution of equations (8) and (9) for S(a) in equation (19), the solution of the problem involves the integration of a complicated function of a'. An exact integration is tedious, and approximate integration techniques are commonly employed.[3] (See appendix A.) With the aforementioned integration techniques, a solution a(t) is obtained in the form:

$$(a - \alpha_1) = (a_O - \alpha_1)e^{-t/\tau_{\alpha_1}} \tag{20}$$

where

$$\alpha_1 = \text{equilibrium radius defined by } S_e$$

$$\tau_{\alpha_1} = \text{relaxation time, characteristic time for approach}$$
$$\text{to equilibrium as growth occurs from } a_O \text{ to } \alpha_1. \text{ NOTE:}$$

$$t \to \infty \qquad a \to \alpha_1$$

and

$$t = 0 \qquad a = a_O \qquad \text{as expected.}$$

The exponential dependence on time for a(t) is a result of the basic form of the growth law and the condition of growth toward stable equilibrium. To gain further insight into this solution, a graphical representation has been developed (figure 4). We see a droplet with initial radius a_O (a_O is the radius of the condensation nucleus) growing by condensation toward the

$$(a - \alpha_1) = (a_0 - \alpha_1)\, e^{-t/\tau}$$

a_0 = INITIAL RADIUS

a = INSTANTANEOUS RADIUS

α_1 = EQUILIBRIUM RADIUS

τ = RELAXATION TIME AT α_1

$$\tau \propto \left(\frac{ds}{da}\right)^{-1}\Big|_{a=\alpha_1}$$

RELATIVE HUMIDITY

S_e

α_1 a a_0

Figure 4. Approach to Stable Equilibrium for an Unsaturated Environment

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equilibrium radius α_1. The instantaneous radius $a(t)$ is defined by equation (20) involving the relaxation time, τ_{α_1}, which represents the time for approach to α_1. The analytical form of τ_{α_1} is in appendix A and takes the form

$$\tau_{\alpha_1} = K(\alpha_1 + \ell)(8\pi\alpha_1^4 - 211.8\, n_2 \alpha_1) / \left[8\pi(1-\psi)(\alpha_1 - \alpha_2)(\alpha_1 - \alpha_3)(\alpha_1 - \alpha_4)\right] \quad (21)$$

The numerical value of τ_{α_1} rests upon the values K, ℓ, n_2, ψ, α_1, α_2, α_3, and α_4. The parameters, K and ℓ, can be considered a priori constants independent of variations in ψ and d. The amount of acid, n_2, in the droplet of interest must be independently specified thereby acting as a constraint on growth. Once ψ is specified, the equilibrium diameter α_1 along with α_2, α_3, and α_4 are established. The variables α_1, α_2, α_3, and α_4 represent solutions to the quartic expression in radius (see appendix A, equation (3A)) and are derivable once ψ is established. Consequently, as ψ and n_2 are named, all other variables in equation (21) become known and calculation of τ_{α_1} is completed. Computations for τ_{α_1} are performed for values of ψ (RH) ranging from 10% to 98% and n_2 ranging from approximately 0.30 E-15 to 0.74 E-12 moles of acid, and are displayed in table 2.

Fortunately, the growth toward stable equilibrium typifies the growth of phosphorus smoke under tactical conditions and therefore equation (20) should represent an adequate model for the initial formation of a phosphorus smoke cloud. Specifically, a_0 represents the radius of the condensation nucleus introduced earlier, and with an analytical expression for τ_{α_1}, a tabular presentation for relaxation time versus relative humidity is displayed in table 2.

As seen from table 2, numerical results reveal extremely small relaxation times for environments characterized by relative humidity ranging from 10% to 98%. *Orders of magnitude for the relaxation times range from 10^{-3} to 0.90 seconds.*

In other words, for the case of unsaturated environments, *acid droplets attain equilibrium with the environment almost instantaneously, and the assertion of diffusional equilibrium under tactical conditions is valid.* As a result, acid droplets can be said to "track" with the environment, a condition conducive to a strong relationship between droplet properties and environmental properties.*

As developed in appendix B, the relaxation time τ is inversely proportional to the slope of the saturation ratio curve, evaluated at the point of equilibrium. Mathematically,

$$\tau_{\alpha_1} \alpha \; a \left(\frac{\partial S}{\partial a}\right)^{-1}_{a = \alpha_1} \quad (22)$$

where

$$S = S(a)$$

---

*Assuming the time of combustion, time of chemisorption, and time of hydration is negligible.

Table 2.   Relaxation Times for Approach to Equilibrium As a Function
of Relative Humidity and Moles of H_3PO_4 (N)

RH / N_2	10%	20%	35.8%	40%	50%	60%	70%	80%	90%	98%
$.29 \times 10^{-15}$	$.34 \times 10^{-4}$	$.51 \times 10^{-4}$	$.69 \times 10^{-4}$	$.82 \times 10^{-4}$	$.10 \times 10^{-3}$	$.13 \times 10^{-3}$	$.24 \times 10^{-3}$	$.48 \times 10^{-3}$	$.14 \times 10^{-2}$	$.17 \times 10^{-1}$
$.10 \times 10^{-14}$	$.58 \times 10^{-4}$	$.97 \times 10^{-4}$	$.14 \times 10^{-3}$	$.16 \times 10^{-3}$	$.20 \times 10^{-3}$	$.29 \times 10^{-3}$	$.46 \times 10^{-3}$	$.94 \times 10^{-3}$	$.29 \times 10^{-2}$	$.36 \times 10^{-1}$
$.5 \times 10^{-14}$	$.15 \times 10^{-3}$	$.24 \times 10^{-3}$	$.34 \times 10^{-3}$	$.38 \times 10^{-3}$	$.52 \times 10^{-3}$	$.75 \times 10^{-3}$	$.12 \times 10^{-2}$	$.25 \times 10^{-2}$	$.78 \times 10^{-2}$	.10
$.34 \times 10^{-13}$	$.50 \times 10^{-3}$	$.75 \times 10^{-3}$	$.11 \times 10^{-2}$	$.13 \times 10^{-2}$	$.17 \times 10^{-2}$	$.24 \times 10^{-2}$	$.41 \times 10^{-2}$	$.80 \times 10^{-2}$	$.26 \times 10^{-1}$	.37
$.14 \times 10^{-12}$	$.12 \times 10^{-2}$	$.18 \times 10^{-2}$	$.27 \times 10^{-2}$	$.30 \times 10^{-2}$	$.41 \times 10^{-2}$	$.61 \times 10^{-2}$	$.10 \times 10^{-1}$	$.2 \times 10^{-1}$	$.65 \times 10^{-1}$	.94 S.

With this identification for τ, it is realized that as the slope of the curve becomes large (steep), the relaxation time becomes small; and with inspection of figure 1, one concludes that characteristic relaxation times for unsaturated environments (RH < 100) are of extremely small magnitude. Another qualitative feature of table 2 is the strong correlation between moles of solute and relaxation time, τ. Specifically, the larger the condensation nuclei (moles of solute) the greater the relaxation time, τ, indicating a longer period for growth toward stable equilibrium. This circumstance is evidenced in equation (19) where the time t(a) is inversely proportional to the difference $S_e - S(a)$. The difference is greater for droplets containing larger moles of solute, resulting in longer periods of time for approach to equilibrium. An alternate perspective is obtained from the dilution effect. In equilibrium, all droplets tend to have the same acid concentration. For larger moles of solute, a greater addition of water is necessary in order to achieve the same degree of dilution and therefore the greater relaxation times.

With a valid relationship between relative humidity and equilibrium drop size, yield factors for a phosphorus smoke may be ascertained.

VII. YIELD FACTOR VERSUS RELATIVE HUMIDITY FOR PHOSPHORUS SMOKE.

Yield factor may be defined as the ratio of final mass to initial mass. In the case of phosphorus smoke, the initial mass corresponds to the amount of red or white phosphorus burned, and the final mass is determined by the mass content of the smoke cloud. The mass of the smoke cloud is the result of four basic reactions: combustion, chemisorption, hydration, and condensation.[9]

Each reaction represents an addition of mass to the initial phosphorus burned. Combustion results in an addition of oxygen whereas chemisorption, hydration, and condensation add water to the system. The estimated size of the condensation nuclei accounts for the addition of oxygen and water due to combustion, chemisorption, and hydration. The specification of drop size through the developed model, with knowledge of condensation nuclei, theoretically accounts for water addition through condensation and, therefore, the determination of the mass of the smoke cloud is uniquely determined by the drop sizes defined by the model. Obviously, drop sizes are relative humidity-dependent and consequently yield factors will be relative humidity-dependent.

To initiate the quantitative analysis for yield factors, consider the following three-step reaction accounting for combustion, hydration, and condensation.

$$P_{4(s)} + 5O_{2(v)} \xrightarrow{\text{combustion}} P_4O_{10(v),(S)} + 6H_2O_{(v)} \xrightarrow{\text{chemisorption}} 4H_3PO_{4(\ell)}$$
$$\text{(condensation nuclei)}$$

$$(23)$$

$$+ nH_2O \xrightarrow{\text{condensation + hydration}} H_3PO_{4(eq)} \quad \text{(drop sizes determined by model)}$$

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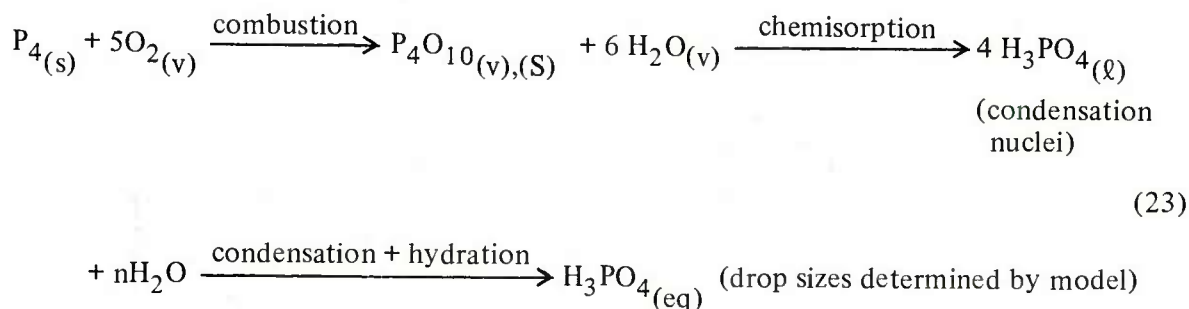
Therefore, for each P_4 complex burned, a $(4H_3PO_4)$ complex is generated representing the condensation nucleus for further growth. From a mass bookkeeping point of view, generation of the smoke cloud is equivalent to generation of the condensation nuclei, nature "picking up the mass tab" for condensation. In order to generate the ith condensation nucleus, consisting of $4H_3PO_4$ complexes, a specific amount of P_4 must be burned. The following algorithm is used: let the mass of the ith condensation nucleus be represented by M_i, then the number of $4H_3PO_4$ complexes contained in the ith condensation nucleus, denote it N_i, is given by

$$N_i = \frac{M_i}{M_{(4H_3PO_4)}} \tag{24}$$

Since for each $4H_3PO_4$ complex one P_4 complex must be burned, then N_i is identically the number of P_4 complexes needed to generate the ith condensation nucleus. This establishes the initial mass burned needed to generate the ith condensation nucleus.

Therefore, the yield factor due to the ith droplet (CN + growth) is given by:

$$Y_i = \frac{\frac{4\pi}{3} a_i^3 \left[\rho_{eff} \right]}{N_i M_{P_4}}, \tag{25}$$

where

$$\rho_{eff} = (\% H_3PO_4 + \% H_2O)/(\% H_3PO_4/\rho H_3PO_4 + \% H_2O/\rho H_2O)$$

where

a_i = radius of the ith droplet at the specified relative humidity

$\% H_3PO_4$ and $\% H_2O$ = percent acid and water in the droplet at that relative humidity

Finally, with knowledge of f_i representing the relative frequency of the ith condensation nucleus,* by taking a weighted average over all condensation nuclei, the total yield factor as a function of relative humidity may be written as

$$YF (RH) = \sum_i f_i 4\pi a_i^3 \left(\rho_{eff}/3N_i M_{P_4} \right) \tag{26}$$

The numerical results are displayed graphically in figure 5 and table 3. *Yield factors range from 3.8 to 16 for RH's ranging from 10% to 90%. The greatest proportion of growth occurs in the region defined by RH > 80%. The augmentation of mass is considerable and indicates the importance of condensation in the determination of yield factors for hygroscopic smokes such as phosphorus smoke.*
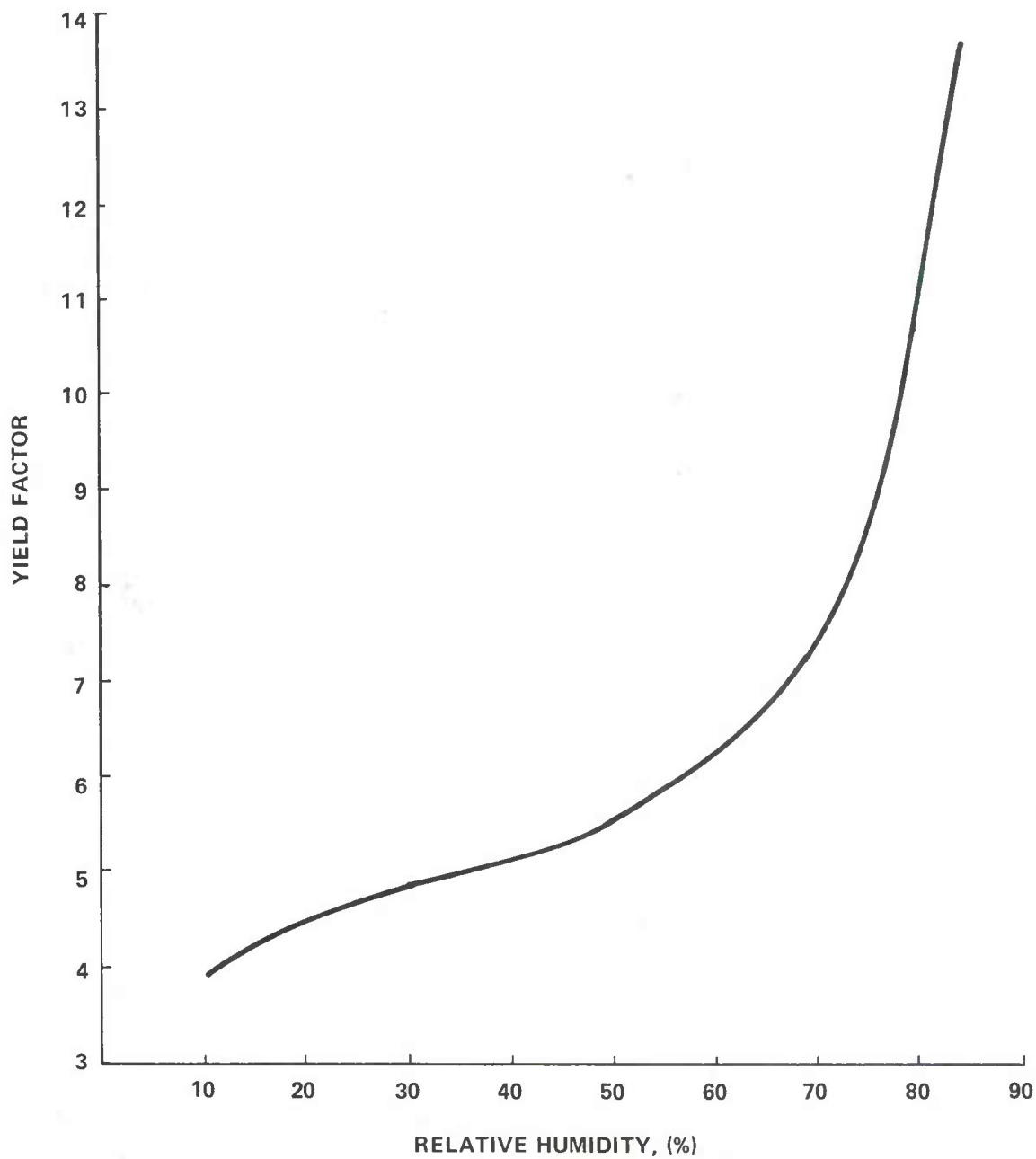
Figure 5.   Yield Factors of a Phosphorus Smoke As
a Function of Relative Humidity

Table 3. Yield Factors of a Phosphorus Smoke As
a Function of Relative Humidity

YF	3.82	4.42	4.91	5.04	5.36	5.97	7.13	9.33	16.29
RH	10%	20%	35.8%	40%	50%	60%	70%	80%	90%

VIII. CONCLUSIONS.

It has been concluded that:

1.   With knowledge of the condensation nuclei size distribution of an oxidized phosphorus, the droplet size distribution of a phosphorus smoke can be confidently predicted.

2.   The relative increase in droplet diameter is solely dependent on relative humidity and is uniform for all acid droplets in a phosphorus smoke. The relative increase in diameter, referenced to the condensation nucleus diameter, is 1.5, 2, and 3 for relative humidities 70%, 90%, and 98%.

3.   The change in droplet diameter concomitant with a change in relative humidity is a monotomically increasing function of relative humidity and the greatest proportion of growth occurs in the region defined by RH >80%.

4.   Droplet acid concentrations of a phosphorus smoke can be effectively ascertained through the size prediction model, thereby providing information on the optical properties of a phosphorus smoke.

5.   The diameter of a phosphoric acid droplet can be *explicitly* expressed as a function of relative humidity and condensation nucleus diameter with sufficient accuracy.

6.   Relaxation times for approach to equilibrium under condensational growth are generally less than 1 second for a phosphorus smoke; consequently, the phosphoric acid droplets should "track" with the environment under tactical conditions.

7.   Theoretical yield factors are nonlinearily dependent on relative humidity and vary from 3.89 to 16.29 at relative humidities 10% and 90%, respectively, for a phosphorus smoke.

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GLOSSARY

a	Solution droplet radius
a_o	Initial radius of solution droplet
a', b'	Empirical functions of relative humidity
d	Solution droplet diameter
d_c	Condensation nucleus diameter
d_{cg}	Geometric mean diameter of condensation nuclei size distribution
D_{eff}	Effective diffusion coefficient; a surface effects parameter
M_1	Molecular weight of solvent (water)
M_i	Mass of ith condensation nucleus
n_1	Moles of solvent (water)
n_2	Moles of solute (H_3PO_4)
P	Actual environmental vapor pressure (water)
P_{so}	Equilibrium vapor pressure
P_d	Vapor pressure over droplet
R	Universal gas constant
RH, ψ	Relative humidity
S_d	Droplet saturation ratio
S_e	Environmental saturation ratio
T	Temperature
t	Time
V_1	Mole volume of solvent
V_2	Mole volume of solute
X_1	Mole fraction of solvent
X_{1eff}	Effective mole fraction of solvent
YF	Yield factors
σ'	Surface tension of droplet
σ	Standard deviation of size distribution
α_i	Equilibrium diameter
ℓ	Surface effects parameter
ρ'	Density of bulk solution
$\rho\ell$	Density of diffusing vapor
$\rho_{eq}^{(\infty)}$	Equilibrium vapor density of environment
ρ_{eff}	Effective density of solution droplet
τ	Relaxation time

GROWTH INTEGRAL

Approximate integration of growth integral for approach to stable equilibrium; relaxation time τ.

With
$$t(a) = \frac{\rho_\ell}{\rho_{eq}(\infty)\,\text{Deff}} \int_{a_o}^{a} \frac{(a'+\ell)\,da'}{S_e - S(a)} \tag{1A}$$

substitution for $S(a)$ given by equation 6 results in the following integrand involving the variable a only:

$$t(a) = K \int_{a_o}^{a} \frac{(a'+\ell)\,da'}{S_e - e^{\left[.23\times10^{-6}/d - \ln\left(1 + \frac{216n_2}{\pi a^3 - 427.8n_2}\right)\right]}}$$

where

$$K = \frac{\rho_\ell}{\rho_{eq}(\infty)\,\text{Deff}} \ .$$

Now, since $.23 \times 10^{-6}/d \ll 1$ for diameters of interest, the approximation $e^X = 1 + x$ may be applied to $S(a)$ resulting the form,

$$S(a) = (1 + .23\times10^{-6}/d)\left[\frac{1}{1 + \frac{216n_2}{\pi d^3 - 427.8n_2}}\right]$$

After standardizing $S(a)$ into a proper fraction, the time integrand becomes,

$$t(a) = K \int_{a_o}^{a} \frac{(a'+\ell)\,da'}{S_e - \frac{(a+.11\,N\,10^{-6})(8\pi a^3 - 319.8n_2)}{36.4\,\pi a^4 - 963.69n_2 a}}$$

and with the additional standardization of the time integrand we arrive at;

$$t(a) = K \int_{a_o}^{a} \frac{(a'+\ell)(8\pi a^4 - 211.8n_2 a)\,da'}{8\pi(S-1)a^4 - .88\times10^{-6}\pi a^3 + (427.8n_2 - 211.8n_2 Sa + 47.06\times10^{-6}n_2} \tag{2A}$$

To evaluate this complex integrand, follow the given procedure:

By factoring $8\pi(s-1)$ from the denominator, a quartic expression   (4th order polynomial in a) is realized where;

$$t(a) = \frac{K}{8\pi(S-1)} \int_{a_o}^{a} \frac{(a'+\ell)\,(8\pi a^4 - 211.8\,n_2 a)\,da'}{a^4 - \dfrac{.88 \times 10^{-6}\pi}{8\pi(s-1)}\,a^3 + \left(\dfrac{427.8\,n_2 - 211.8\,n_2 S}{8\pi(S-1)}\right)a + \dfrac{47.06 \times 10^{-6}n_2}{8\pi(S-1)}}$$

Now the quartic expression $a^4 + ba^3 + ca + d$ may be rewritten as the product of its factored roots, i.e.,

$$a^4 + ba^3 + ca + d = (a - \alpha_1)(a - \alpha_2)(a - \alpha_3)(a - \alpha_4)$$

where α_1, α_2, α_3, and α_4 are obtained by solving the equation $a^4 + ba^3 + ca + d = 0$. (This is easily handled by most pocket calculators.) Therefore, the time integrand becomes:

$$t(a) = \frac{K}{8\pi(S-1)} \int_{a_o}^{a} \frac{(a'+\ell)\,(8\pi a^4 - 211.8\,n_2 a)\,da'}{(a-\alpha_1)(a-\alpha_2)(a-\alpha_3)(a-\alpha_4)} \qquad (3A)$$

where α_1, α_2, α_3, and α_4 satisfy the polynomial equation,

$$8\pi(S-1)a^4 - .88 \times 10^{-6}\pi a^3 + (427.8\,n_2 - 211.8\,n_2 S)a + 47.06 \times 10^{-6}n_2 = 0.$$

Now $t(a)$ represents the time at which the droplet, experiencing condensational growth, achieves its final radius a. For the problem of approach to stable equilibrium, the final radius is the radius of equilibrium and is given by the condition that $S_e = S(a)$. This relationship is satisfied by the values of a such that $a = \alpha_1$, $a = \alpha_2$, $a = \alpha_3$, and $a = \alpha_4$. Now only one of these four solutions is positive and real, call it α_1, and it represents the equilibrium radius. Thus the upper limit of integration in equation (3A) is identical to the final equilibrium radius α_1. However, when $a = \alpha_1$, the denominator of the integrand in equation (3A) is zero and the integrand is consequently infinite. In other words, due to the singular nature of $1/(a-\alpha_1)$, the magnitude of the integrand is sharply peaked in the neighborhood of $a = \alpha_1$, as seen in the figure. From a time viewpoint, this implies that for growth toward stable equilibrium the greatest portion of time is accounted for in the neighborhood of equilibrium. This statement is confirmed by the modified growth law which states that the change in radius is greatest when the difference in saturation ratio is greatest. Near equilibrium we have a minimum in this difference and, therefore, a minimum in the rate of change in radius. Therefore, a long time is spent in condensational growth near equilibrium. Thus, to a good approximation, all terms in the integrand are mathematically constant as compared to the highly

singular term $1/(a - \alpha_1)$. Therefore, a mean value approach is in order and all terms may be brought outside the integral evaluated at α_1 except for the term contributing to the largeness of the integrand $\left(1/(a - \alpha_1)\right)$. Therefore, we may mathematically write:

$$t(a) \simeq \frac{K(\alpha_1 + \ell)(8\pi\alpha_1^4 - 211.8n_2\alpha_1)}{8\pi(S-1)(\alpha_1 - \alpha_2)(\alpha_1 - \alpha_3)(\alpha_1 - \alpha_4)} \int_{a_0}^{a} \frac{da'}{(a - \alpha_1)} \quad .$$

$a = \alpha_1$

a
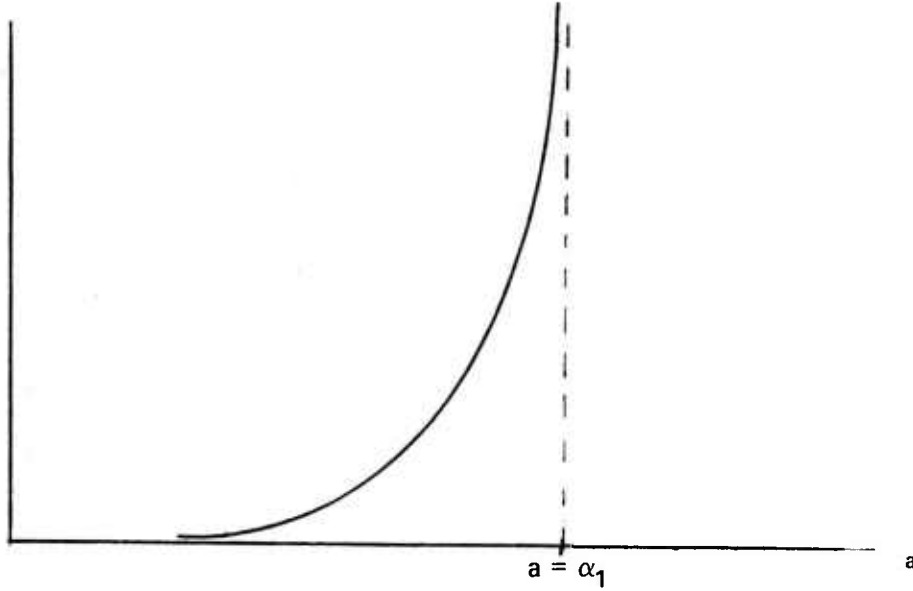
Figure. Relative Magnitude of Integrand

Now $S - 1 < O$ for unsaturated environments and we may rewrite $t(a)$ as,

$$t(a) \simeq -\tau_{\alpha_1} \ln \frac{a - \alpha_1}{a_0 - \alpha_1} \tag{4A}$$

where

$$\tau_{\alpha_1} = \frac{K(\alpha_1 + \ell)(8\pi\alpha_1^4 - 211.8n_2\alpha_1)}{8\pi(|S-1|)(\alpha_1 - a_2)(\alpha_1 - \alpha_3)(\alpha_1 - \alpha_4)} \quad . \tag{5A}$$

Now equation (4A) may be reformed into its exponential equivalent giving us the growth solution to stable equilibrium characterized by the relaxation time τ_{α_1} given by equation (5A), where

$$(a - \alpha_1) = (a_0 - \alpha_1)e^{-t/t_{\alpha_1}}$$

Appendix A

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APPENDIX B

ANALYTICAL EXPRESSION FOR RELAXATION TIME

With

$$t(a) = K \int_{a_0}^{a} \frac{(a' + \ell) \, da'}{S_e - S(a)}$$

and the understanding that this integrand is dominated in the vicinity of $a = \alpha_1$, then we may approximate this integrand in the following manner:

Since this integrand is dominated near $a = \alpha_1$, we can expand $S(a)$ in a Taylor series expansion about α_1 retaining only the first term,

Therefore

$$S(a) = S(\alpha_1) + \left(\frac{\partial S}{\partial a} \right)_{a = \alpha_1} (a - \alpha_1) + \, ' \, ' \, '$$

and therefore

$$t(a) = K \int_{a_0}^{a} \frac{(a' + \ell) \, da'}{S_e - S(\alpha_1) - \left(\dfrac{\partial S}{\partial a} \right)_{a = \alpha_1} (a - \alpha_1)}$$

But

$$S(\alpha_1) = S_e \rightarrow t(a) = K \int_{a_0}^{a} \frac{(a' + \ell) \, da'}{- \left(\dfrac{\partial S}{\partial a} \right)_{a = \alpha_1} (a - \alpha_1)}$$

Again using the mean value approach of appendix B we obtain

$$\tau_{\alpha_1} \approx \frac{K(\alpha_1 + \ell)}{\left(\dfrac{\partial S}{\partial a} \right)_{a = \alpha_1}}$$

and, therefore, the relaxation time is inversely proportional to the slope of the saturation curve evaluated at the radius of equilibrium.

APPENDIX C

ACID CONCENTRATIONS OF PHOSPHORIC ACID DROPLETS
AS A FUNCTION OF RELATIVE HUMIDITY

Relative humidity	H_3PO_4 Acid
%	%
98	6
90	23
80	38
70	49
60	58
50	65
40	70
36	72
20	78
10	82
0	100

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